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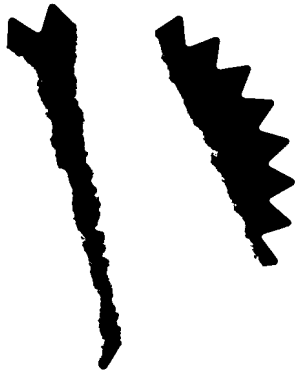
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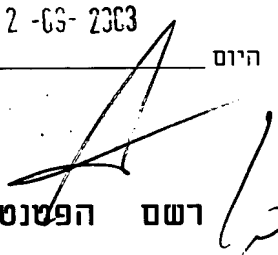
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Application for Patent

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IMPROVED ABRASIVES FOR CHEMICAL-MECHANICAL  
POLISHING APPLICATIONS

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חלקיקי שחיקה משופרים לתהליכי ליטוש כימי-מכני

IMPROVED ABRASIVES FOR CHEMICAL-MECHANICAL  
POLISHING APPLICATIONS

## **IMPROVED ABRASIVES FOR CMP APPLICATIONS**

### **FIELD OF THE INVENTION**

This invention relates to wafer planarizing chemical mechanical polishing (CMP ) systems.

### **5 BACKGROUND OF THE INVENTION.**

The quest for ever greater miniaturization of electronic interconnect devices imposes stringent and challenging processing standards in general, and in particular in the areas of wafer flatness or planarity. The challenge stems, inter  
10 alia, from the multitude of differing metals/materials used at the various levels. Specifically, copper which is greatly favored as interconnect metal because of its attractive electrical conductivity and low cost, presents special planarity challenges, due to its chemical reactivity that makes it prone to oxidation / erosion, believed by many to be the cause of dishing.

15 To achieve optimum planarization, the industry increasingly relies on mechanical chemical polishing ( CMP ) at each manufacturing level.

Broadly, there are two types of CMP processes:

A. Slurry-based CMP compositions, wherein abrasive particles along with other ingredients are dispersed in aqueous/solvent media, and are delivered onto  
20 a pad, typically made of polyurethane or polyurethane composites. The surface to be planarized is rubbing against the rotating pad resulting in a leveling action via removal of protruding/uneven matter.

B. Fixed abrasive pads, wherein abrasive particles are embedded in the polishing pad. Fixed polishing systems are gaining popularity because they lead to better planarity. Also, fixed abrasive systems generate less waste, as they do not require delivery of extraneous slurry.

5 Abrasive materials utilized both in slurry suspensions and fixed abrasive pads, are typically a blend of particulate metal oxide particles, generally selected from the group of oxides of silicon, cerium, aluminum, titanium, and others.

Slurry-based systems present difficulties, some of which are.

1. The slurry suspensions are prone to stratification/settling that tends to  
10 make the suspension non-homogeneous and unstable that can lead to uneven, non uniform slurry delivery, resulting in uneven planarity. This is caused at least in part, by the multiplicity of metal oxide particles in the slurry blend, with each metal oxide having individual and potentially dissimilar surface properties.

15 2. Slurry particles tend to "stick " to the polished wafer, leading to particulate surface contamination, that makes the wafer difficult to clean satisfactorily.

3. Spent or waste slurry particles can clog the grooves of the polishing pads,  
20 again resulting in uneven slurry delivery and unsatisfactory planarization.

Referring to fixed-abrasive pad systems, they tend to yield improved planarity, compared to slurry-based systems, but because of the hydrophobic nature of the abrasives embedded in the polymer matrix, are often prone to poor  
25 wettability.

The prior art recognizes the need for improved abrasive particles, to better serve the industry's challenging needs. This need is reflected in part by US patents # 6582623 to Grumbine and # 6592776 to Wang, that are indicative of the more recent prior art. They disclose abrasives that are "surface-modified" via  
30 organic silanes, and/or via nitrogen-containing compounds, such as benzotriazole

(referred to as "film-forming agents"), and at least one silane compound. The thus surface-modified abrasives are reported to afford tailoring a given polishing composition for a specific task, to achieve a desired polishing rate, to suit the nature of material to be polished, etc. The surface-modified abrasives are also  
5 said to reduce agglomeration and settling of the slurry dispersions. Surface modifiers are contained in a solvent which, when added to the dispersion leads to the bonding of the surface-modifying moiety to the abrasive particle.

### SUMMARY OF THE INVENTION

10 The present invention provides a novel, structurally improved, abrasive agent with advantageous overall properties, comprising improved surface properties resulting, inter alia, in enhanced wettability, dispersability and bonding.

The invention will be disclosed mainly by the following aspects:

15

1. An abrasive agent that consists of particles comprising more than one metal oxide, e.g. particles that comprise two metal oxides, for example  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .

2. An abrasive agent that consists of metal oxide particles coated at  
20 least partially with an extraneous metal or metal bearing layer.

3. Abrasive agents that consist of abrasive particles comprising more than one metal oxide and are coated at least partially with an extraneous metal or metal bearing layer are also within the scope of the present invention.

25 While the novel particle of this invention is of particular interest in the field of chemical-mechanical polishing, it potentially can be embodied for polishing of metals and non-metals in general, for manufacturing cutting tools, industrial coatings, and a host of others.

The abrasive agent of the invention comprises particles that produce more uniform, more stable dispersions, when compounded into a CMP slurry. The  
30 agent also reduces metal, especially copper, dishing.

The abrasive agent of the invention leads to improved, more durable fixed- abrasive pads, with reduced scratching. Another advantage of the abrasive agent of the invention is to minimize the problem of spent slurry particles depositing on the wafer surface, hindering wafer cleanliness and wafer  
5 cleanability.

According to one aspect, the above, as well as other improvements are provided by coating the abrasive particles at least partially with a metallic or  
10 metal bearing layer, prior to their use in CMP slurries, or prior to their inclusion into fixed-abrasive pads. The metallic layer can be achieved by any one of numerous existing coating processes, such as vapor - phase metallization, flame, plasma, electroless deposition from aqueous systems, and a host of other methods.

15 Also, the invention contemplates the metal bearing substance that is deposited onto or into the abrasive particle ( also referred to at times, interchangeably, as "grain"), to preferably different than the metal component constituting the "body " or "core " of the metal oxide particle or grain, upon which the metal or metal oxide is deposited on.

20 Thus, according to another aspect, the abrasive agent consists of particles that are composites containing two or more metallic oxides on, or in, in the same particle, as opposed to particles consisting of a single metal oxide, as generally practiced by the prior art. Such composite particles may be obtained via gaseous compositions. An abrasive particle or grain, that is a composite of multiple  
25 oxides of differing metals, will lead to polishing benefits. As an example, the invention contemplates abrasive particle composites of  $\text{SiO}_2$  and  $\text{TiO}_2$  on the same grain.

#### **DETAILED DESCRIPTION OF THE INVENTION.**



As mentioned above, the general concept of one aspect of the present invention focuses on increasing the surface energy of abrasive particles or grains by enveloping them, partially or completely, with a metallic layer or film. In this application, the terms "layer", "film" and "coating" are used interchangeably.

5 Also, the term "partially covered" , is understood in this invention to cover partial coverage of the abrasive particles with a layer of material, as well as spotty, "patchy" coverage of the abrasive particles. Such patchy coverage by the metal bearing layer can be as little as a small fraction of the total particle surface.

10 As to the term "completely covered", it implies in this invention to denote at least a 50 % coverage of particle area exposed to metallization.

The thus metallized, metal-coated grain results in a novel abrasive particle entity, leading to a multitude of advantages, some of which have been mentioned previously.

15 It is envisioned that the statistical distribution of the coated abrasive particles will by necessity encompass a broad and varying range of surface coverages, i.e. particles that are partially covered, as well as particles that are completely covered, affording an abrasive blend with adjustable properties, ranging from properties of essentially uncoated abrasives, to properties of  
20 essentially metal-covered particles, and properties that are "in-between".

Metallic or metal bearing coatings or films, as used in this invention, include metals or metalloids at zero valence state, and/or metal oxides, metal hydroxides, water-insoluble metal compounds in general, as well as mixtures thereof. Also, above metallic coatings will be less than "pure", as it is often  
25 impractical to industrially produce metal bearing films that are devoid of impurities.

The metal-bearing layer comprises at least one metal selected from the group consisting of Cu, Ti, Fe, Sn, Pb, Ta, Mo, Wo and Nb.

It is further noted that certain preferred embodiments of the invention will  
30 be best served with coatings of metals at zero valence state, yet other preferred

embodiments will opt for coatings of metal oxides, hydroxides, and the like, or mixtures thereof.

Referring to the thickness of metal-bearing films or layers, they can cover a very broad range, from a monolayer to several Angstroms. As to the upper  
5 thickness limit of the metal bearing substance, it will generally not exceed the size or diameter of the grain itself. The choice will be guided by the desired function of the coating or film. For example, while the surface energy of the coated particles can be enhanced, and wettability / adhesion to a binder improved, with films or coatings whose thickness is in the monolayer range,  
10 impacting the mechanical, chemical characteristics of the coated abrasive may require layer thicknesses of several Angstroms or small fractions of microns.

Depending on the nature of the metal in the metallic coating, the layer covering the abrasive particles will undergo chemical attack when exposed to the slurry suspension. The invention therefore envisions recycling, remetallizing and  
15 recoating abrasives as needed. Also, the invention further contemplates the use of alloy coatings, with the composition of the alloy being optimized for a given process, taking into consideration resistance to chemical attack by the slurry, and the principal function of the proposed layer, i.e. whether mechanical, chemical, etc. For the sole purpose of illustration, one would consider minimization of  
20 dishing to be a chemical or galvanic function, whereas reduction of scratching is viewed as a mechanical function.

In a further embodiment of the invention, one may opt for slurry suspensions that are binary mixtures, combining unmetallized abrasives with metalized abrasives, i.e. abrasives with altered outer surfaces covered with  
25 metallic or metal bearing layers.

In a still further embodiment, the above aforementioned binary slurry suspension will comprise particles of metal powders/particles, or particles of metal oxide powders. This, to accentuate a desired chemical or mechanical effect, over and above what is imparted by the coated abrasive.

The present invention further foresees combining metallized or metal - coated abrasives with an organic layer. The organic layer or film can precede the metallic layer or top it. Examples of such potential organic layers or films are disclosed in US # 6582623 B1, herein incorporated by reference.

5 One skilled in the art will have at his disposal numerous techniques for covering the grain with metal bearing layer or layers. Broadly, though not limitingly, such techniques will involve deposition of the film from gaseous environments, or from aqueous/semi aqueous compositions, with the latter often considered a preferred embodiment, as being more throughput-friendly. For  
10 example, deposition of the metallic layer from colloidal compositions is deemed a particularly attractive embodiment, because they can also serve to redeposit the metallic or metal bearing layers as they become depleted in use.

The present invention additionally envisions incorporation of metal-bearing colloids into the slurry suspensions themselves, with the continuous, in-  
15 situ forming / reforming of the films over the grains, during the progress of the polishing operation. The choice of such colloids will have to be guided by their compatibility with the slurry environment, especially as to the pH of the latter. GB # 417340, # 792624, 713211 to Johnson, and WO 0155092 to Rhodia, disclose colloids that can be helpful.

20 When opting for colloidal, preferably aqueous or semi-aqueous colloidal suspensions, as a means to coat or recoat the abrasive particles with the desired metallic layer, one skilled in the art will generally expose the abrasives to be coated via the colloidal suspension, with energetic agitation/stirring of the to-be-coated abrasive particles, while contacted with the colloid. This can be  
25 followed by draining, water rinsing, and drying of the coated abrasives. Drying the coated abrasives is generally desirable before they can be incorporated into fixed-abrasive pad binders.

Furthermore, when copper is the metallic layer of choice, the abrasives can be contacted with an aq. cupric copper solution that comprises  
30 chemical reducing agents yielding copper metal, cuprous hydroxide, or mixtures

thereof. Spent copper waste solutions will be of special interest, because of economic and environmental considerations. Specifically, and illustratively, spent etchants with their high concentrations of cupric ammonium chlorides and carbonates can be advantageously and economically used to coat or recoat abrasives with copper-bearing layers. it is noted that the prior art considers copper dishing a phenomenon of copper erosion by the polishing fluid, and US# 6537144 proposes the presence of copper metal on the polishing pad to minimize dishing. "Copperized" abrasives of this invention will eminently serve this purpose.

10

#### CLAIMS:

1. An abrasive agent comprising abrasive particles, said particles being in the form of a composite material comprising more than one metal oxide.
- 15 2. An abrasive agent according to claim 1, wherein said abrasive particles are in the form of a composite material made of two metal oxides.
3. An abrasive agent according to claim 2, wherein said composite material comprises  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .
4. An abrasive agent comprising metal oxide abrasive particles, said particles  
20 being coated at least partially with an extraneous metal or metal bearing layer.
5. An abrasive agent according to claim 4, wherein said abrasive particles are further coated at least partially with a polymer layer.
6. A chemical mechanical polishing (CMP) composition comprising an abrasive agent according to claim 1.
- 25 7. A chemical mechanical polishing (CMP) composition comprising an abrasive agent according to claim 4.
8. The CMP composition of claim 7 wherein the metallic or metal bearing layer include metals or metalloids at zero valence state, metal oxides, metal hydroxides, water-insoluble metal compounds, as well as mixtures thereof.

9. The CMP composition of claim 8 wherein the metal-bearing layer comprises at least one metal selected from the group consisting of Cu, Ti, Fe, Sn, Pb, Ta, Mo, Wo and Nb.
10. The CMP composition of claim 8 wherein the metal-bearing coating is a  
5 metal oxide.
11. A fixed abrasive CMP pad comprising abrasive particles according to claim 1.
12. A fixed abrasive CMP pad comprising abrasive particles according to claim 4.
13. A fixed abrasive CMP pad comprising abrasive particles according to claim  
10 4, wherein said particles are completely covered with a metal bearing coating.
14. A CMP slurry comprising a CMP composition according to claim 6.
15. A CMP slurry comprising a CMP composition according to claim 7.
16. A CMP slurry comprising a CMP composition according to claim 7, wherein said abrasive particles are completely covered with metal a bearing coating.
- 15 17. A method of manufacturing an integrated circuit comprising using a composition according to claim 6.
18. A method of manufacturing an integrated circuit comprising using a composition according to claim 7.
19. An abrasive particle that is a single composite of at least two metal oxides.
- 20 20. An abrasive agent comprising abrasive particles, said particles being in the form of a composite material comprising more than one metal oxide and being coated at least partially with an extraneous metal or metal bearing layer.